A Precise Gas Chromatographic Method Using ECD Detection for the Measurement of Nitrous Oxide in Vehicle Exhaust

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Extended Abstract # 32

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INTRODUCTION

In its climate change programs, the State of California has identified nitrous oxide from motor vehicles as a significant source of greenhouse gases (see, for example, References 1-3). The early development of the electron capture or ECD detector (Reference 4) has revolutionized much of analytical chemistry for environmental analyses, including the analysis of nitrous oxide. The measurement of nitrous oxide using gas chromatography combined with the ECD detector provides both excellent selectivity due to good column availability and high sensitivity from the use of the ECD detector. A report of the initial development of the method used in this paper provides insight into the novel approaches using ECD detection that are still evolving (Reference 5).

Selected reports involving vehicle exhaust measurements of nitrous oxide using gas chromatography coupled with ECD detection (References 6-9) involve studies on a variety of vehicle types including both gasoline-fueled and diesel-fueled vehicles. Reference 6 provides a mechanism for the formation of nitrous oxide in exhaust from carbon monoxide and nitric oxide on the vehicle catalyst at elevated temperatures. In this mechanism, nitrous oxide formation occurs during the vehicle cold start phase when the catalyst is warming up (at 280C - 330C), but ceases when the catalyst is warmed up. High nitric oxide in the exhaust favors the formation of nitrous oxide.

$$2NO + CO = N_2O + CO_2 \quad \text{(low temperature)}$$
$$NO + CO = \tfrac{1}{2}N_2 + CO_2 \quad \text{(high temperature)}$$
$$N_2O + CO = N_2 + CO_2$$

Other measurement methodologies, particularly Fourier Transform Infrared Spectroscopy (FTIR), have also been used for this purpose (Reference 10-13). A new low level, nondispersive infrared analyzer is currently being tested (Horiba Instruments, MEXA-7000) for vehicle exhaust studies. In general, the levels of nitrous oxide in vehicle exhaust have been decreasing as the technologies controlling the vehicle emissions have improved, and dilution factors are being reduced to extend the lifetime of current instrumentation. In a review of nitrous oxide emissions from vehicles (Reference 14), the authors note that the mechanism for nitrous oxide production from the reaction of nitric oxide and carbon monoxide within the vehicle exhaust system would make it likely that future vehicles would have even lower nitrous oxide emissions. Therefore, as nitrous oxide levels continue to decrease in vehicle exhaust, it will be important to maintain high precision and accuracy for these measurements.

This paper will discuss the GC-ECD method actively used by the California Air Resources Board (CARB) for determination of nitrous oxide in vehicle exhaust, as well as the approaches for using this methodology for vehicle emission studies. It is noted that this instrumental method is actually configured as part of a more complex gas chromatograph, designed to measure simultaneously the Greenhouse Gases carbon dioxide, carbon monoxide, methane, and nitrous oxide. Data from vehicle exhaust emission testing illustrating the application of the nitrous oxide analysis is provided.

EXPERIMENTAL METHOD

This CARB methodology (see Reference 15) uses a Varian Model 3800 Gas Chromatograph modified with a complex valving configuration that isolates the nitrous oxide peak via a middle cut or “heart cut” methodology, separating the nitrous oxide from both the lighter interfering gases, including oxygen, and the heavier interfering gases, Freon and hydrocarbon compound. (See Figure 1). Instrument details are provided in Table I which gives instrument setup information for several reported procedures used in vehicle exhaust studies as a means of illustrating the variety of test procedures used for this purpose. The use of ascarite and sodium sulfate by Graham et al (Reference 9) to scrub interferents is designed to permit use of the small diameter PLOT column. The chromatogram (See Figure 2) contains only three peaks; carbon dioxide, nitrous oxide, and sulfur hexafluoride. Both the carbon dioxide and the sulfur hexafluoride peaks are chromatographically well separated from the nitrous oxide peak, and there is some “clipping” of the carbon dioxide peak in the present instrument to ensure isolation from the oxygen peak.

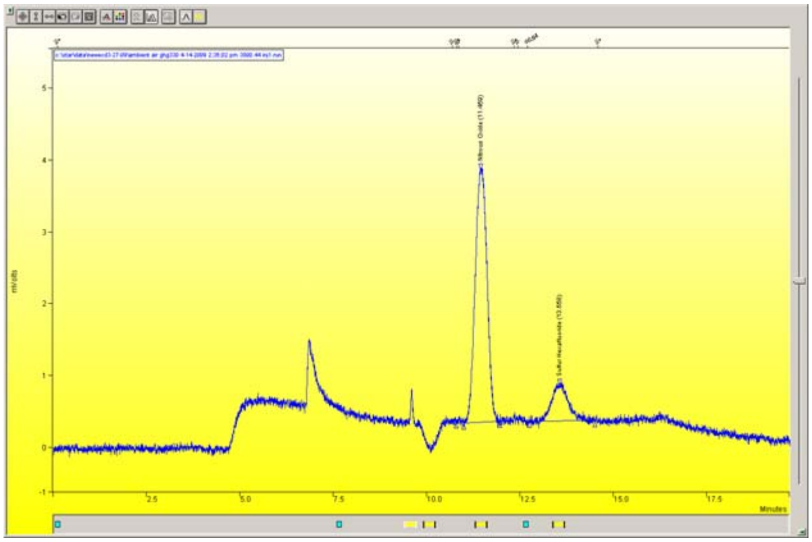
Table 1. Comparative Summary of Some ECD Test Methods for Nitrous Oxide Analysis in Vehicle Exhaust

Test Parameter	**Dasch (1992)**	**Graham (2008)**	**This Work (2010)**
Method Type	Single Backflush	Scrubber/Capillary	Middle Cut
Sample Loop	2.5 cc	0.25 cc	5 cc
Precolumn	OV17, 1/8” x 2’	(Ascarite, NaSO4)	Haysep N, 1/8” x 6’
Analytical Column	Poropak Q, 1/8”x 12’	PLOT Q, 15M x 0.54mm x 40u	Haysep D, 1/8” x 15’, Haysep D, 1/8” x 15’
Column Temperature	Room Temperature	40C	75C
Carrier Gas	CH4/Ar at 50 cc/min	He at 9.7 cc/min	N2 at 20 cc/min,
Makeup Gas		CH4/Ar at 56 cc/min	N2 at 8 cc/min CH4/Ar at 2 cc/min
ECD Temperature	350C	180C	300C – 350C

Gas purity is an important concern for ECD analysis. In this CARB procedure, highly purified, ultrapure nitrogen gas is used both as the chromatographic carrier gas and as the make-up gas for the ^{63}Ni ECD detector. The source of this nitrogen is boil-off from a liquefied nitrogen storage tank which is further conditioned with hydrocarbon and oxygen filters at the gas chromatograph. The detector make-up nitrogen is further blended with an argon-methane gas mixture to form a gas blend that appears to improve the operation of the ^{63}Ni ECD detector by improving the longterm response stability. The argon-methane gas mixture is also filtered with oxygen and hydrocarbon filters at the gas chromatograph.

The temperature of the valves, the heated sample lines, and the GC oven were maintained at 75°C for these tests, although system temperatures in the range 60°C to 80°C have been used successfully. The limiting aspect of the temperature used in this gas chromatograph is not the temperature being used for the nitrous oxide analysis, but the additional requirement of the other Green House Gas analyses in this gas chromatograph and the concern to avoid condensation of the heavier exhaust hydrocarbons that may be present in either the light duty vehicle or the diesel vehicle exhaust samples that are analyzed. Use of a slightly longer column would require higher oven temperatures to maintain an analysis time of 20 minutes. Figure 1 is a typical ambient air chromatogram for this analysis.

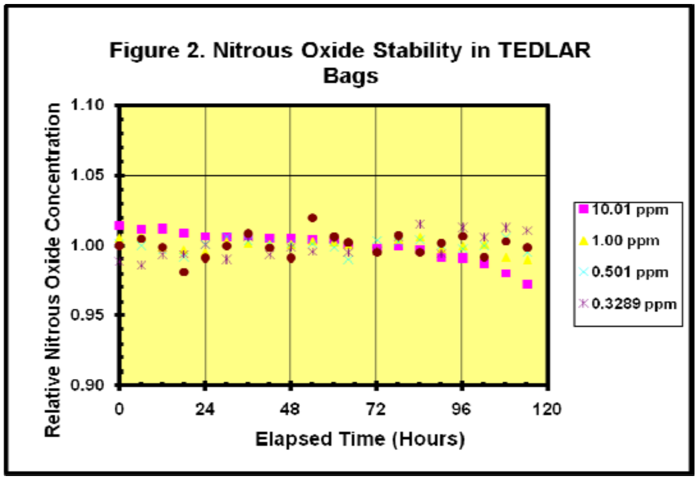
Figure 1. A typical Chromatogram for the Analysis of Ambient Air.



Gas standards used for routine nitrous oxide calibration are at concentrations of 0.5 ppm, 1.0 ppm, and 5.0 ppm (Scott-Marrin, Inc.). It is important that the lower standard be near the ambient air concentration. The concentrations of each standard were verified against a diluted working standard made from a 10 ppm NIST standard. Ambient air is used for daily quality control. The calibration of the nitrous oxide signal from the ECD detector is nonlinear over the extended calibration range (0.01 ppmV to 5.00 ppmV). Both the nitrous oxide calibration coefficients and concentrations are calculated directly in an EXCEL spreadsheet using a second order fit with zero intercept to the calibration data for that day; alternatively, a graphical procedure can be used to derive these coefficients.

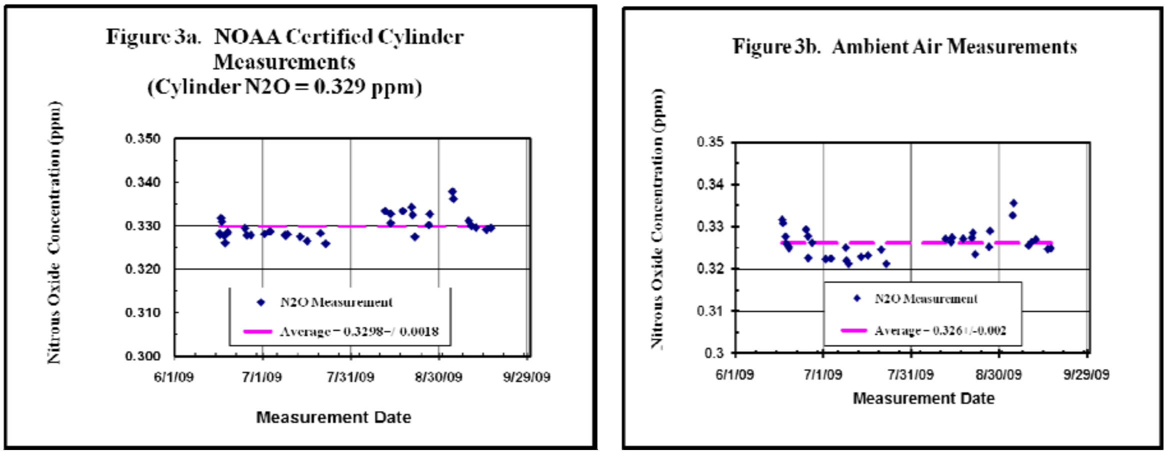
Samples from vehicle dynamometer testing are routinely collected in specially constructed Tedlar bags (about 6 Liter capacity) fitted with Quick Connect fittings (Swagelok Corporation), and are connected directly to the gas chromatograph prior to analysis. The stability of the nitrous oxide in the Tedlar^{TM} bags was found to be at least four days (see Figure 2).

Figure 2. Stability of Nitrous Oxide at various concentrations in TEDLAR Bags



Results for the weekly quality control analysis of ambient air and a low level standard purchased from NOAA are shown in Figure 3. These weekly quality control measurements are the average of five individual and successive readings. The expected background concentration of ambient air in California is about 0.324ppm; The average results shown in Figure 3a over the selected time period was found to be 0.326ppm, with about 2% scatter in the plot. It is surprising that the value comes close to the expected ambient background concentration considering the location of the laboratory near a freeway. The concentration of nitrous oxide in the NOAA certified cylinder was found to be 0.329 ppm; the agreement in this case is gratifying.

Figure 3. Weekly Quality Control Measurements for Nitrous Oxide in Ambient Air and in NOAA Certified Gas Cylinder



The procurement of samples for motor vehicle exhaust testing involves using background air for the dilution of the vehicle raw exhaust stream. This background air is generally taken from the local ambient environment. Since background air contains nitrous oxide as one of its constituents, the background nitrous oxide levels are considered in the calculation of the vehicle exhaust emissions in a complex manner, but basically by subtraction. Nitrous oxide is very stable and exhibits a long lifetime in the atmosphere; it is wise to be aware of the background nitrous oxide levels when making vehicle exhaust measurements. Globally, measurements of ambient concentrations of nitrous oxide have exhibited a slow and steady increase for many years. For example, using GC-ECD techniques, measurements in Hateruma Monitoring Station in Japan from 1996 to 1999 (Reference 22) show nitrous oxide concentrations ranging from 0.313ppmV to 0.315ppmV, with a steady annual increase of 0.64ppb/yr. Weekly data taken at Point Arena, California from 1999 through 2009 (see: http://www.esrl.noaa.gov/gmd/ccgg/iadv/) show a continuing trend with similar increasing nitrous oxide data from a level of 0.315ppmV in 1999 to a level of about 0.324ppmV in 2009. These sets of independent measurements are in good agreement.

At this stage of method development in our laboratory, the nitrous oxide peak is separately integrated for each analysis. As more test experience is gained, it is expected that routine integration by the data program will be probable. Complicating factors in automated peak area integration are two: 1) peak tailing, 2) baseline sloping caused pressure relaxation from improper compensation for valve changes, or 3) detector drift. The contributing problem to the peak tailing is only to the high concentration calibration standards, but not to the vehicle samples. Early use of a high level standard at 10 ppm complicated the interpretation of peak tailing. Even the present use of the 5 ppm standard gives some peak tailing, which must be accounted for in the day-to-day calibration analysis. During very early method development, sample concentrations as high as 6ppm were anticipated, and high nitrous oxide values in the range 2-3 ppm were often observed. However, in this final period of method development, all samples were below 0.6 ppm. The difference is due primarily to the type/age of vehicles tested and to the dilutions required for the diesel samples. The result is a trend in sample concentration that approaches the value of the ambient concentration. This trend is expected to continue unless vehicle sampling procedures change or catalysts change. Detector drift due to contamination is a problem that one faces in all parts of analytical chemistry. The solution is to have the most sensitive detector available or to reduced the noise level of the detector in some manner.

ECD DETECTION

The ^{63}Ni ECD detector commonly being used today is a low level radioactive device that produces an ionizing, electron field within the central cavity of the detector housing. This electron field is modified by the any gas flowing through the detector. The quality of the ECD detector response to the nitrous oxide in the sample depends both on the stability of the detector (which can exhibit day-to-day signal decay) and on the inherent detector noise. In the ECD analysis, the measured electron signal change (or loss) is related to both the electron affinity of the nitrous oxide (an inherent property) and the amount of the sample nitrous oxide that passes through the ionizing field within the detector. The signal loss resulting from the presence of any nitrous oxide found within this field is detected, amplified, and converted. To favor the collection of the preferred high energy electrons in the detection process, highly optimized pulsed electronics are utilized by most vendors.

The signal vs. concentration curve for nitrous oxide in an ECD detector is near linear with the nitrous oxide concentration for about 2-3 orders of magnitude, and nonlinear beyond 3-4 orders of magnitude. Lasa et al., (Reference 16-18), provide theoretical insight into the operation of modern pulsed ECD detectors. These authors indicate that detector linearity and response are related to the fundamental mechanisms of the electron capture process in the gas plasma, which are complex and which are treated in their papers. The resulting signal strength, they add, is also a function of the detector design itself, which is often somewhat empirical or constrained. Some results from the linearity of one ECD detector used at the ARB gave the plots shown in Figure 2.

Figure 4. Partial Comparison of Nonlinear vs Linear Data fits to Nitrous Oxide Concentrations

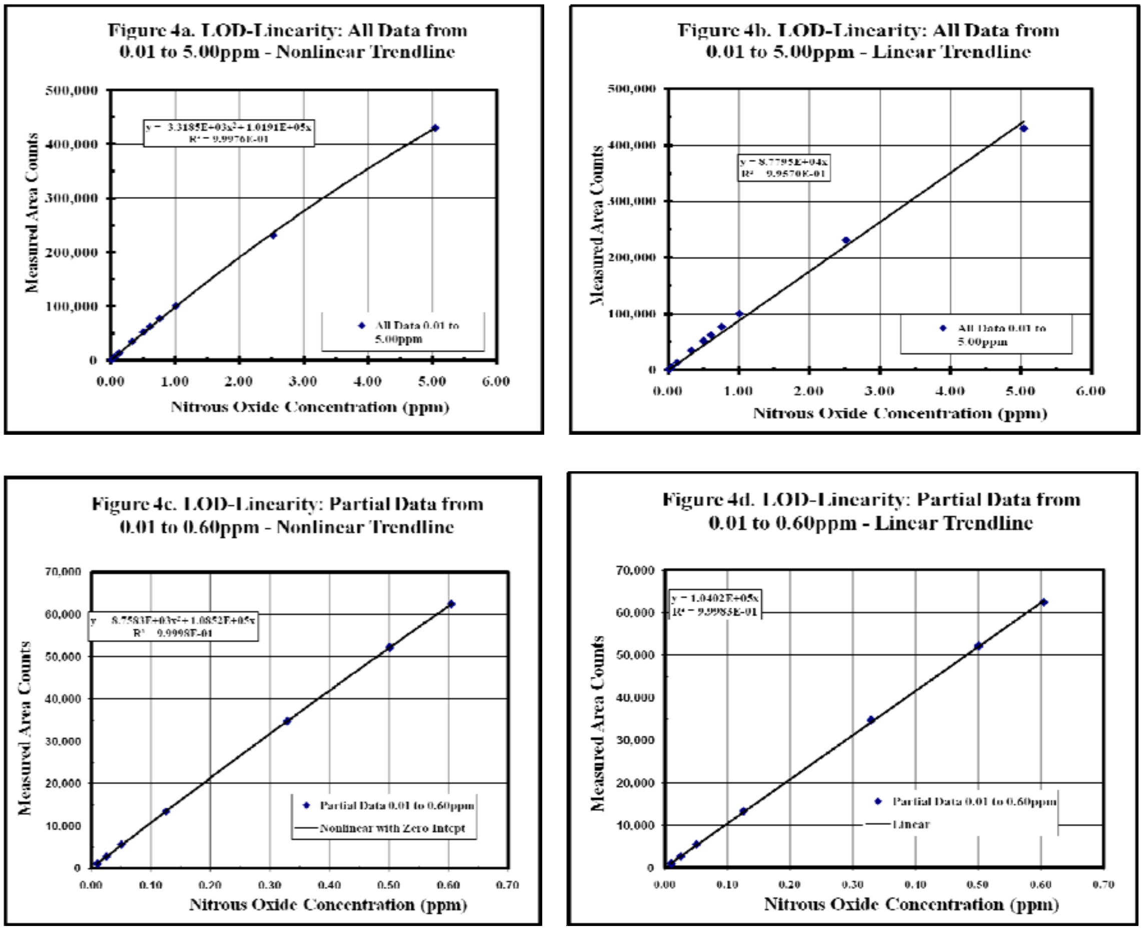


Figure 4a. LOD-Linearity: All Data from 0.01 to 5.00ppm - Nonlinear Trendline

Figure 4b. LOD-Linearity: All Data from 0.01 to 5.00ppm - Linear Trendline

Figure 4c. LOD-Linearity: Partial Data from 0.01 to 0.60ppm - Nonlinear Trendline

Figure 4d. LOD-Linearity: Partial Data from 0.01 to 0.60ppm - Linear Trendline

Table 2. provides a more detailed look at this same linearity data for additional concentration ranges. Both the nonlinear regression and the linear regression are performed with zero intercept. Both data sets in the table do show good consistency for the parameters chosen; and in most cases, one would have difficulty ignoring any of these regressions. However, the major observation in the linear charts is that the regression points do not appear to fit the line as well as the nonlinear fit does for the higher concentrations. While it is not completely appropriate to make one-to-one comparison of a linear and a nonlinear regression, the "visual" and the "calculated" do agree. This observation is borne out by the slightly poorer, yet good quality, R^2 factors from all of the data fits. The overall consistency of the nonlinear fit suggests that a nonlinear fit is the better empirical choice for a ECD detector when measuring nitrous oxide.
As an added note, we have found slightly different parameters for detector nonlinearity over time as we changed from one detector to another. It has been helpful to pay close attention to elimination of leaks to gain best performance from the detectors.

Table 2. Summary of Nonlinear and Linear (with Zero Intercept) Regression Constants for Nitrous Oxide Data from 0.01 ppm to 5.00 ppm.

N2O Range (ppm)	k_1	k_2	R^2	k_1	R^2
0.01 – 5.00	1.019E+5	-3.318E+3	0.99976	0.878E+5	0.99570
0.33 – 5.00	1.019E+5	-3.031E+3	0.99968	0.878E+5	0.99409
0.01 – 1.00	1.084E+5	-8.461E+3	0.99999	1.019E+5	0.99922
0.01 – 0.60	1.085E+5	-8.758E+3	0.99998	1.040E+5	0.99983
0.01 – 0.50	1.086E+5	-8.910E+3	0.99997	1.045E+5	0.99986
0.01 – 0.33	1.089E+5	-9.988E+3	0.99993	1.059E+5	0.99983
0.01 – 0.125	1.119E+5	-39.563E+3	0.99972	1.076E+5	0.99940
0.01 – 0.075	1.083E+5	-8.461E+3	0.99999	1.033E+5	0.99970

Also with regard to ECD detectors, it is known that there are contamination effects within the detector that contribute to various noise current pathways which result in either diminished signal, increased noise, and/or limited dynamic range. The usual cure for contamination is to bake out the detector at an elevated temperature such as 400C for an overnight period or longer while isolating the detector from column flow and purging the detector at high flow rates of nitrogen. Our experience is that high temperature baking can also lead to response loss. However, after exposure to higher temperatures we sometimes observe that the response of the nickel detector decreases, possibly due to the presence of small amounts of oxygen in the gas stream, causing formation of surface nickel oxide which reduces emission of electrons. Whether this problem is due to a small air leak, or is induced by the nature of the vehicle samples, has not yet been defined. The solution has been to minimize the detector bake cycles and the temperature of the bake cycle. Fortunately, the use of Ar/CH_4 in the makeup gas to the detector seems to maintain the performance of the detector longer. Another factor that has been observed may be gaseous contamination within the interstitial confines of the ^{63}Ni structure itself (leading to moderation of the electron energy by trapped molecules) under some circumstances. This issue specifically occurred for hydrogen gas; it has not been evaluated for other gases.

The ECD measurement of nitrous oxide has been shown to have strong temperature dependence, with a suggested optimum performance around 350°C (Reference 19). We have confirmed this trend and periodically use this effect to increase the signal when necessary. It has been reported elsewhere that the nitrous oxide response increases both with increasing detector temperature and with the presence of added “dopants,” such as oxygen at the 100ppm level in the nitrogen carrier gas (Reference 20, 21). This enhancement of the nitrous oxide response factor in the presence of oxygen has been attributed to a series of complex ion-molecule reactions within the detector itself (References 22, 23). Our experience to date is that the presence of any oxygen is detrimental to detector behavior, resulting in loss of response. Attempts to evaluate the use of carbon dioxide and methane as contributing to enhancement of the nitrous oxide signal were unclear and not enough work was performed. What was discovered was that helium leak checking of the instrument led to reduction of an apparent enhancement effect. More needs to be studied here. Other means used to increase the ECD signal, such as use of hydrogen cleaning (Reference 24) which regenerates the original nickel within the detector from the surface nickel oxide, have actually been shown to decrease the signal for a short period, probably due to temporary trapping of hydrogen within the interstitial confines of the nickel, leading to moderation of the energy of the electron emission so that the ^{63}Ni electrons do not have sufficient energy to interact with the nitrous oxide. This effect does subside, leaving a rejuvenated detector. Hydrogen regeneration is a process that must be carefully performed and is not casually recommended since it will not increase the activity of the detector beyond its inherent electron emission capacity. Further, it is so far unclear what conditions are needed to regenerate modern ECD detectors with hydrogen. At times, it may be useful; however, more needs to be done in this area, otherwise, instrument downtime will result.

RESULTS AND DISCUSSION

Using the middle-cut method for nitrous oxide measurement, vehicle samples were obtained from both a low emission vehicle dynamometer and a diesel engine dynamometer. We report below, some results from these studies. In Table 3 and Table 4.

Table 3. Selected Nitrous Oxide Test Data for Low Emission Vehicle Tests

Vehicle Test	**Nitrous Oxide Mode #1**	**Nitrous Oxide Mode#2**	**Nitrous Oxide Mode #3**	**Nitrous Oxide Mode #0**
1	0.328	0.329	0.329	0.329
2	0.433	0.327	0.360	0.332
3	0.455	0.327	0.360	0.328
4	0.342	0.329	0.327	0.335
5	0.349	0.326	0.350	0.331
6	0.351	0.325	0.337	0.332
7	0.375	0.324	0.318	0.333
8	0.387	0.328	0.326	0.339
9	0.348	0.316	0.325	0.325
10	0.367	0.334	0.345	0.344
Average:	**0.374**	**0.326**	**0.338**	**0.333**
Stand. Deviation:	**0.041**	**0.005**	**0.015**	**0.005**
RSD:	**11.0%**	**1.4%**	**4.5%**	**1.6%**

Table 3 provides results for ten low emission vehicle tests from different vehicles and testing conditions. Results from all test modes are included in the table. It is noted that all results are below 0.5ppm for nitrous oxide, indicating that these are low emitting vehicles. Also, the highest measurements were in the Mode#1 sample, as expected. The results from the background bag or the ambient air sample, Mode#0, yielded an average value of 0.333+/-0.005ppm for nitrous oxide. This average is slightly higher than expected.

Table 4. Selected Modal Nitrous Oxide Results for Diesel Engine Dynamometer Tests

N_2O	**Mode #1**	**Mode #2**	**Mode #3**	**Mode #4**	**Mode #5**	**Mode #6**	**Mode #7**	**Mode #8**	**Mode #0**
Test	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
1	0.430	0.384	0.360	0.355	0.377	0.354	0.350	0.340	0.326
2	0.429	0.387	0.364	0.353	0.388	0.351	0.348	0.337	0.326
3	0.433	0.385	0.361	0.351	0.383	0.351	0.349	0.341	0.329
4	0.423	0.379	0.359	0.353	0.375	0.348	0.347	0.341	0.328
5	0.435	0.393	0.369	0.354	0.392	0.350	0.348	0.338	0.329
6	0.431	0.386	0.359	0.352	0.381	0.349	0.345	0.337	0.325
7	0.425	0.376	0.359	0.354	0.377	0.351	0.351	0.341	0.329
8	0.434	0.388	0.366	0.355	0.393	0.356	0.353	0.339	0.328
9	0.433	0.382	0.360	0.351	0.383	0.349	0.348	0.340	0.326
10	0.428	0.383	0.357	0.354	0.374	0.350	0.349	0.339	0.330
Avg:	**0.430**	**0.384**	**0.361**	**0.353**	**0.382**	**0.351**	**0.349**	**0.339**	**0.328**
Std Dev:	**0.004**	**0.005**	**0.004**	**0.001**	**0.007**	**0.002**	**0.002**	**0.002**	**0.002**
RSD:	**0.91%**	**1.25%**	**1.08%**	**0.39%**	**1.83%**	**0.68%**	**0.62%**	**0.00%**	**0.47%**

Table 4 provides results for ten diesel engine dynamometer test on a truck refrigeration unit. The test cycle included 8-modes and a background sample, Mode#0. The modal tests were all conducted on different days over a period of weeks. There is strong consistency in the data. The average for the background sample, Mode#0, is 0.328+/-0.002ppm. A reasonable value for ambient air using this procedure.

The diluted diesel engine dynamometer samples were diluted about 100x, and the diluted gasoline exhaust samples were diluted about 5x. Actual emissions of nitrous oxide are related by a complex difference between the concentrations in the sample and in the dilution air. The emissions were not calculated for these tests. The results are in agreement with other results from this instrument. One point that should be noted, since emissions are determined from the small differences between the diluted sample and the ambient air concentrations, this analysis requires higher-than-usual precision. The current nitrous oxide limit of detection, LOD, for the instrument of 0.003 ppm is sufficient to provide reliable emissions calculations for vehicle testing.

ECD detectors have sometimes received a very negative reputation for difficulty in use. This reputation may be due to lack of full concern for leak prevention. A leak anywhere in the gas handling system…starting at the pressure regulator for the cylinder gases used for service to the instrument, continuing through the often large number of connections used for hookup of gases to the instrument, and ending up with all of the internal connections within the instrument…are all sources of air leaks that can affect ECD detector performance over weeks and months.

The discussion further emphasizes the following regarding maintenance of methods with ECD detectors.

Table 5. Design, Prevention, and Maintenance – The Path to ECD Success

1. A helium leak check of the instrument prior to use and as needed is desirable – all connections can leak; oxygen should be kept out of the detector for best performance.
2. The use of clean gases is essential for detector longevity – the removal of oxygen and of hydrocarbons will help to maintain the detector.
3. The use of final cleaning of the column nitrogen and the makeup nitrogen with a catalytic scrubber is being evaluated.
4. The use of GC valves w/gold-plated ferrules and purged housings are used to limit impact of small air leaks.
5. High flow rates should be maintained at the detector to purge the detector cavity.
6. The ECD detector should be baked as needed, but not excessively – this effect still being evaluated.
7. It was found that signal continuity is better using a Ar/CH4 mixture – there is more to be determined here.
8. Operation of the GC in an isothermal mode for best baseline stability.
9. Gas chromatography – use of the middle cut technology to remove both light gases (oxygen, nitrogen, methane) and heavy gases (hydrocarbons and Freons) prior to analysis appears to have no negative impacts.

SUMMARY

The data and discussion presented here suggest the following.

1. The ECD method for nitrous oxide has the needed sensitivity and range for use in vehicle exhaust studies.
2. The ECD method for nitrous oxide is very usable in the laboratory.
3. By design, the middle-cut column technology reduces potential complications from interfering species that may reach the ECD detector.
4. ECD detector does require paying routine attention to system cleanliness and to leaks; good analytical practices result in good data.
5. This ECD method currently measures ambient air within 2% under the best conditions.
6. A nonlinear calibration curve,2nd order with zero intercept, affords the best fit over entire measurement range of the ECD detector.
7. A second order regression can be readily carried out in EXCEL for automated concentration calculations.

8. The expected enhancement with the presence of carbon dioxide and methane was not found; but more work needs to be done here. The expected enhancement with the presence of oxygen (100ppm) only led to detector failure.
9. Contaminants from vehicle exhaust do reduce the response of the ECD detector; use of Ar/CH4 mixture at 10-20% appears to help the detector longevity by helping it to recover its detectivity. The loss is small, typically about 1-2%; this may be an interstitial effect.

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KEYWORDS

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